

# AMENDED SPECIFICATION

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## PATENT SPECIFICATION

517,333



Convention Dates  
(United States)

Corresponding Applications  
in United Kingdom

Aug. 7, 1937.  
July 12, 1938.

No. 21873/38 }  
No. 21874/38 } dated July 23, 1938.

(One Complete Specification Left under Section 91 (2) of the Patents and Designs Acts, 1907 to 1932.)

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## COMPLETE SPECIFICATION

### Improvement in Catalyst and Process for Olefine Oxidation

We, CARBIDE AND CARBON CHEMICALS CORPORATION, of 30, East Forty-second Street, New York, State of New York, United States of America, a Corporation organised under the laws of the State of New York, United States of America, (Assignees of **RAYMOND WILSON McNAMEE** and **CHARLES MABRY BLAIR**, citizens of the United States of America, residing respectively at 1032, Columbia Boulevard and 1507—A, Virginia Street, both of Charleston, State of West Virginia, United States of America), do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention provides improvements in the process of making olefine oxides by the direct catalytic oxidation of olefines by means of molecular oxygen. Specifically, it provides surface catalysts of increased activity, ruggedness and life for use in such processes.

When olefine oxides are formed by causing olefines to combine directly with molecular oxygen in the presence of a surface catalyst at temperatures between about 150° and 400° C., silver alone, or activated by the addition of small amounts of gold or copper or iron, is a very suitable catalyst to employ. However, we have now discovered that silver surface catalysts can be made more rugged and durable, more active, and of greater useful life in the process by incorporating in them limited amounts of certain alkalis. Not all alkaline substances are suitable. and extensive tests have shown that the truly useful promoting agents are the peroxides, oxides and hydroxides of barium, strontium, and, to a lesser extent, of lithium. Compounds of alkali metals

which form stronger bases than lithium hydroxide or of alkaline earth or earth metals whose hydroxides are weaker bases than strontium hydroxide have either less beneficial effect or are actually harmful to the silver surface catalysts. Barium oxide, peroxide and hydroxide are by far the most desirable promoting agents, followed, in order of preference, by the peroxides, oxides and hydroxides of strontium and lithium. Of the stronger bases, sodium hydroxide has less permanent beneficial effect as a promoter, and potassium and caesium hydroxides are actually detrimental in their action. Weaker bases, such as calcium and magnesium hydroxides (or oxides), appear to act as promoting materials for the silver catalysts, but the augmented activity is accompanied by a sharp decrease in the chemical efficiency of the process, and such activation as is secured is therefore undesirable.

The present invention, therefore, provides an active surface catalyst capable of effecting the direct oxidation of olefines to olefine oxides, for example ethylene to ethylene oxide, preferably at temperatures between about 150° C. and about 400° C., characterized in that it comprises essentially silver together with one or more of the peroxides, oxides or hydroxides of barium, strontium and lithium to increase its active life, ruggedness and catalytic activity.

The reaction by which olefines, especially ethylene, are caused to combine directly with molecular oxygen to form the corresponding olefine oxide (ethylene oxide) was first shown by Lefort to proceed at temperatures of about 150° to about 400° C. Also as shown by Lefort, the reaction proceeds at either atmospheric pressure or at increased or decreased pres-

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sures, and any proportion of the olefine  
 and oxygen or air (or other oxygen-con-  
 taining gas) can be used. The surface  
 catalyst used in carrying out the reaction  
 5 can be disposed in the reaction vessel in  
 any desired way which will insure the  
 necessary contact of the reactants with the  
 catalyst, and we prefer to employ granular  
 supporting materials, pellets, small rods,  
 10 or some similar expedient providing an  
 extended surface for this purpose. Arti-  
 ficial silica filter stone, sandstone or one  
 of the commercially available ceramically  
 bonded alumina refractory materials,  
 15 when crushed and screened to a con-  
 venient size, are examples of suitable  
 catalyst supports.

The essential constituent of the surface  
 catalyst is silver, and with it we incor-  
 20 porate a lesser amount of the promoting  
 material. For example, we may use the  
 promoting substances in amounts of from  
 about 2% to about 40% by weight of the  
 silver contained in the catalyst, and, in  
 25 most cases, about 10% is desirable. The  
 quantity of silver contained in the cata-  
 lysts supported on inert materials may  
 vary over a wide range, but, in general,  
 we prefer to use from about 5% to about  
 30 60% by weight. The size of the  
 catalyst support is not essential, and  
 can be chosen to suit the conditions  
 of operation.

The following specific examples will  
 35 serve to illustrate the invention:

In each of the tests described in the  
 succeeding examples, the various promot-  
 ing agents were evaluated by determining  
 the maximum production of ethylene  
 40 oxide by silver surface catalysts contain-  
 ing the added substances at temperatures  
 of operation within the temperature range  
 of 200° to 300° C. This method of evalua-  
 tion readily permits the selection of those  
 45 promoters which are most desirable from  
 practical considerations.

Each test was conducted by passing a  
 mixture of ethylene and air containing  
 5% of ethylene at the rate of 100 liters per  
 50 hour over the catalyst contained in a tube  
 having an internal diameter of one inch.  
 The catalysts were supported on irregular  
 particles of porous artificial silica filter  
 stone or similar support sized to between  
 55 4 and 8 mesh screens. In each case,  
 approximately 250 cc. of the supported  
 catalyst were used. The catalyst in the  
 tube was maintained at temperatures  
 between 200° and 300° C., and the maxi-  
 60 mum overall yield of ethylene oxide which  
 was produced within this range was deter-  
 mined by analysis of the issuing gases. In  
 every case, the reactant gases were care-  
 fully purified before being admitted to the  
 65 catalyst chamber.

#### EXAMPLE 1.

An unpromoted catalyst was prepared  
 by precipitating silver oxide through the  
 reaction of aqueous solutions of silver  
 nitrate and sodium hydroxide in roughly 70  
 stoichiometrical proportions. The precipi-  
 tated silver oxide was washed free of  
 alkali and soluble salts and dried.

A mixture of 120 parts by weight of the  
 support, crushed and sized as described 75  
 above, together with 60 parts by weight of  
 silver oxide and 100 parts by weight of  
 water, was heated in an open vessel and  
 stirred vigorously until the water was  
 evaporated. 80

The maximum yield of ethylene oxide  
 obtained with this catalyst under the con-  
 ditions set forth was 35%, based on the  
 weight of the ethylene admitted. After  
 750 hours of operation, the maximum 85  
 yield obtainable with this catalyst was  
 22%. When small quantities of ethylene  
 dichloride (equal to about 0.05% by  
 volume of the total gas mixture) were  
 admitted with the purified gases in an  
 effort to improve the chemical efficiency of  
 90 the reaction obtained with this catalyst,  
 its activity decreased after 8 hours to a  
 maximum yield of only 2%.

#### EXAMPLE 2.

A catalyst was prepared as described in  
 Example 1 with the exception that to the  
 mixture of silver oxide, water and catalyst  
 support were added 6 parts by weight of  
 barium dioxide. 95

The maximum yield of ethylene oxide  
 secured with this catalyst under the con-  
 ditions described was 44%. After 750  
 hours, its activity was unchanged. A  
 similar catalyst was used continuously in  
 105 the production of ethylene oxide for more  
 than 7 months, ethylene dichloride in  
 small amounts (less than 0.1% by volume  
 of the total gases) being introduced from  
 time to time to improve the chemical effi-  
 110 ciency of the reaction, and it was found  
 to have retained its initial activity.

Other catalysts were prepared in which  
 20 and 40 parts by weight of silver oxide  
 and 2 and 4 parts by weight of barium 115  
 dioxide, respectively, were supported on  
 120 parts by weight of crushed and sized  
 porous silica stone. These catalysts each  
 gave the same initial yield of ethylene  
 oxide as that previously described. 120

Another catalyst was made up of 20  
 parts by weight of silver oxide and 2 parts  
 by weight of barium hydroxide supported  
 on 120 parts by weight of crushed and  
 sized porous silica stone. This catalyst 125  
 possessed a maximum activity, under the  
 same conditions as have been described,  
 equivalent to an overall yield of ethylene  
 oxide of 42%.

## EXAMPLE 3.

A catalyst was prepared as in Example 1 in which 60 parts by weight of silver oxide and 6 parts by weight of strontium hydroxide were deposited on 120 parts by weight of the crushed and sized support.

When tested under the conditions described above, this catalyst produced ethylene oxide in amounts equal to a yield of 38%. Its activity was not materially impaired by protracted service, nor decreased significantly by the use of the minute quantities of ethylene dichloride used to improve the chemical efficiency of the reaction.

## EXAMPLE 4.

A catalyst identical with that of Example 3 in which lithium hydroxide replaced the strontium hydroxide possessed an activity equivalent to a maximum yield of ethylene oxide of 24%.

## EXAMPLE 5.

A catalyst in which potassium hydroxide replaced the strontium or lithium hydroxides of Examples 3 or 4 was prepared and tested under the conditions previously described. This catalyst was almost entirely inactive, and the maximum yield of ethylene oxide obtainable with it was only 0.1%.

Cesium hydroxide also appeared to act as a catalyst poison, and catalysts capable of allowing more than traces of ethylene oxide to be formed under the test conditions could not be made using this substance.

## EXAMPLE 6.

A catalyst was made as described in Example 1 in which 20 parts by weight of the silver oxide and 2 parts by weight of calcium hydroxide were deposited on 120 parts by weight of the crushed and sized support.

This catalyst initially produced ethylene oxide with an overall yield of 28% under the test conditions. The efficiency was very low, and it was not found possible to secure acceptable yields of ethylene oxide with practicable chemical efficiency under any conditions using this catalyst.

Magnesium and aluminum hydroxides, when substituted for the calcium hydroxide in similar catalysts, suffered the same defects as were exhibited by the calcium-containing catalyst and, additionally, gave maximum initial yields of ethylene oxide which were much lower than were obtained with calcium hydroxide.

In the foregoing description, the greatly improved usefulness of the catalytic materials of this invention has been demonstrated. This is not only due to the higher initial yields which are generally obtained with the promoted catalysts, but

also to their longer life. A catalyst formed of silver containing 10% of barium dioxide and supported on granular ceramically bonded alumina was found not to have decreased in activity (as determined by the yield of ethylene oxide produced; after seven months continuous operation. A catalyst containing no promoter but formed of the same amount of silver disposed on the same kind of support was found to have decreased 35% in activity after 750 hours operation. Furthermore, the non-promoted catalysts have no practical resistance to poisons, including such selective poisons as ethylene dichloride, which may be used to improve the chemical efficiency of the oxidation reaction. Therefore, the promoted catalysts are not only less susceptible to accidental loss of activity, but they are capable, when used with inhibitors, of producing ethylene oxide with desirably high efficiencies.

The improved catalysts shown herein are not only much less sensitive to poisoning than are the unpromoted catalysts, but they are also more resistant to other deactivating conditions. For example, a catalyst formed of silver oxide together with 10% barium dioxide supported on granular porous silica was intentionally severely overheated so that it lost nearly all of its activity. An unpromoted silver catalyst was similarly treated. On resuming operation at normal conditions, the promoted catalyst regained most of its activity, while the unpromoted catalyst did not.

In the foregoing comparisons between the new catalysts of this invention and unpromoted silver catalysts, the silver in the catalyst compared was as nearly as possible in the same physical condition. The activating or promoting agents of this invention always show an improvement over the same silver used alone, but the extent of improvement achieved varies according to the form of the silver used. Also, in those catalysts high in total silver content the degree of activation produced by this invention is, in general, less than where the silver content is lower. However, in each case the promoted catalyst is definitely preferable because of its increased life, ruggedness, resistance to catalyst poisons and resistance to the effects of sudden general or local overheating.

Variations in the method of obtaining the new catalysts are possible. For example, the peroxides of the metals named are the preferred activating agents, but alternative successful methods of making the promoted catalysts may include the incorporation in the catalyst

of the metal hydroxide with or without hydrogen peroxide. Mixtures of two or more of the promoting agents may, of course, be used.

- 5 The eventual chemical conditions of the promoting metal is not known, but examinations of barium-containing catalysts after use always show the barium to be in a water-soluble, strongly alkaline condition. This is entirely unexpected, since the catalysts in operation are always in contact with carbon dioxide, and the quantitative formation of barium carbonate would appear to be inevitable. A possible explanation seems to be that a hitherto unknown complex containing barium, silver and oxygen is formed, which decomposes when treated with water, giving barium hydroxide and an oxide of silver.
- 10 Most salts of the metals are definitely without promoting action or are detrimental to the catalysts so long as they exist in the catalyst as such. Some few salts, however, can be converted, during use of the catalyst, into the strongly alkaline condition above described, and are then active as promoters. Thus, barium carbonate is found surprisingly to change into this condition when mixed with silver oxide and used under ordinary operating conditions. Also barium chloride, in the presence of sufficient ethylene oxide and moisture, reacts to give the same result.

- 20 The operation of the oxidation process in which the novel catalytic materials of this invention are used may follow that shown by Lefort as hereinbefore described. The physical conditions may be varied and selected to suit the exact mode of operation chosen. The ethylene oxide, or other olefine oxide, produced can be recovered in any suitable manner by absorption, condensation or in solution.

- 40 We are aware of Specification No. 509,183, which claims a method of producing olefin oxides which comprises sub-

jecting a gaseous mixture comprising an olefin and oxygen to contact with catalyst consisting of a carrier which is essentially aluminium oxide, and silver, and selectively absorbing the olefin oxide from the gaseous mixture and further claims such a method in which the catalyst consists of a carrier, which is essentially aluminium oxide promoted by one of the metals of the alkali and alkaline earth metal groups, and silver.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the direct oxidation of olefines to olefine oxides, which consists in passing olefines in admixture with oxygen or gases containing oxygen over a catalyst consisting essentially of silver together with one or more of the peroxides, hydroxides or oxides of barium, strontium or lithium at a temperature between 150° and 400° C.

2. A process as claimed in claim 1, in which the catalyst comprises one or more of the peroxides, oxides or hydroxides of barium, strontium and lithium in an amount less than that of the silver.

3. A process as claimed in claims 1 and 2, in which the catalyst comprises a barium oxide equal to between about 2% and about 40% by weight of the silver.

4. A process as claimed in claims 1—3, in which the catalyst comprises about 10% of barium dioxide.

5. The process of making olefine oxides as hereinbefore particularly described and claimed.

6. Olefine oxides whenever prepared or produced by the process claimed.

Dated this 22nd day of July, 1933.

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